PATENT SPECIFICATION

(19)

(54) METHOD OF MANUFACTURING A ZEOLITIC ADSORBENT

(71) We, UOP INC., a corporation organized under the laws of the State of Delaware, United States of America, of Ten UOP Plaza, Algonquin & Mt. Prospect Roads, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The field of art to which the claimed invention pertains is zeolitic adsorbent production. More specifically, the invention relates to a method of manufacturing an adsorbent having improved characteristics for the separation of an extract component from a feed mixture comprising an extract component and a raffinate component.

Our copending GB Patent Application No. 19016/74 (Serial No. 1,466,577) claims a method of manufacturing a solid adsorbent for the separation of para-xylene from a mixture of C_8 aromatic hydrocarbons which method comprises the steps of:

(a) contacting a precursor mass containing type X or type Y zeolite and amorphous material with an aqueous sodium hydroxide solution at first ion exchange conditions to effect the addition of sodium cations to the zeolite structure;

(b) treating the sodium-exchanged mass at second ion exchange conditions to effect the essentially complete exchange of sodium cations with barium or barium and potassium cations; and

(c) drying the resulting exchanged mass at conditions to reduce the loss on ignition at 900°C to less than 10 wt.%.

It will be seen that the only disclosure of specific exchanges in step (b) in that specification is the essentially completely exchange of sodium cations by barium cations or barium and potassium cations.

We have discovered that ion-exchanging particles of a precursor mass comprising type X or type Y zeolite with an aqueous solution of sodium hydroxide, prior to the ion exchange not only with Ba or Ba+K cations but with cations of Groups IA, IIA and IB in general, produces an adsorbent possessing faster adsorption-desorption rates when used in processess to separate an extract component from a raffinate component both of which appear in feed mixtures fed to the processes. The reason for this is not entirely understood but it is hypothesized that the ion-exchange of the precursor mass with aqueous sodium hydroxide replaces extraneous non-sodium cations, such as H+ or Group IIA cations, present in the precursor mass and occupying exchangeable sites within the zeolite thereby permitting higher amounts of the selected cations to be added during a subsequent ion-exchange step.

According to the present invention therefore there is provided (subject to the disclaimers hereinafter) a method of manufacturing a solid adsorbent which method comprises the steps of: (a) contacting a precursor mass comprising X or Y zeolite with an aqueous sodium hydroxide solution at first ion exchange conditions to effect the addition of sodium cations to the zeolite structure; (b) treating the sodium-exchanged mass at second ion exchange conditions to effect the essentially complete exchange of sodium cations with cations of one or more metals selected from Group IA, Group IIA, and Group IB of the Periodic Table of Elements; and (c) drying the material at conditions to reduce the LOI at 900°C. to less than 10 wt.%.

The adsorbent produced by the method of the invention is useful in such adsorp-

tive separation processes as: a process for the separation of pinene isomers, a process for the separation of butene-1 from other C_4 mono-olefins, a process for separating tetra-alkyl substituted monocyclic aromatic hydrocarbon isomers, and a process for the separation of the para-isomer from a hydrocarbon feed mixture comprising at least two bi-alkyl substituted monocyclic aromatic isomers, the isomers having from 8 to about 18 carbon atoms per molecule. In particular, adsorbents produced by the method of the invention are useful for selectively adsorbing all of the xylene isomers in a feed stream to the substantial exclusion of ethylbenzene to enable recovering of high purity ethylbenzene (see our copending GB Patent Application No. 29044/76 — Serial No. 1,550,391), and also for separating components of a feed mixture comprising a ketose and an aldose (see our copending GB Patent Application No. 22240/77 — Serial No. 1,574,915).

The type X and Y crystalline aluminosilicates or zeolites herein contemplated can be described as a three-dimensional network of fundamental structural units consisting of silicon-centered SiO_4 and aluminum-centered AlO_4 tetrahedra interconnected by a mutual sharing of apical oxygen atoms. The space between the tetrahedra is occupied by water molecules and subsequent dehydration or partial dehydration results in a crystal structure interlaced with channels of molecular dimension.

Thus, the crystalline aluminosilicates are often referred to as molecular sieves and separations performed with molecular sieves are generally thought to take place by a physical "sieving" of smaller from larger molecules appearing in the feed mixture. In the separation of aromatic hydrocarbon isomers, however, the separation of the isomers apparently occurs because of differences in electrochemical attraction of the different isomers and the adsorbent rather than on pure physical size differences in the isomer molecules.

In hydrated form, the preferred crystalline aluminosilicates generally encompass those zeolites represented by the formula 1 below:

Formula 1.
$$M_{2/n}O : Al_2O_3 : wSiO_2 : yH_2O$$
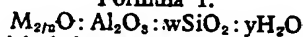
where "M" is a cation which balances the electrovalence of the tetrahedra and is generally referred to as an exchangeable cationic site, "n" represents the valence of the cation, "w" represents the moles of SiO_2, and "y" represents the moles of water. The cations may be any one of a number of cations which will hereinafter be described in detail.

Adsorbents comprising the type X structured and type Y structured zeolites are especially preferred for the adsorptive separation of aromatic hydrocarbon isomers. These zeolites are described and defined in U.S. Patents 2,882,244 and 3,120,007 respectively. The terms "type X structured" and "type Y structured" zeolites as used herein shall include all zeolites which have general structures as represented in the above two cited patents.

The type X structured zeolite in the hydrated or partially hydrated form can be represented in terms of mole oxides as shown in formula 2 below:
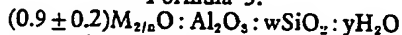
Formula 2.
$$(0.9 \pm 0.2)M_{2/n}O : Al_2O_3 : (2.5 \pm 0.5)SiO_2 : yH_2O$$
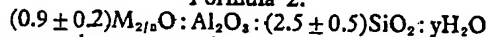
where "M" represents at least one cation having a valence of not more than 3, "n" represents the valence of "M" and "y" is a value up to 9, depending upon the identity of "M" and the degree of hydration of the crystal. The cation "M" may be one or more of a number of cations such as the hydrogen cation, the alkali metal cation, or the alkaline earth cations or other selected cations, and is generally referred to as an exchangeable cationic site.

The type Y structured zeolite in the hydrated or partially hydrated form can be similarly represented in terms of mole oxides as in formula 3 below:

Formula 3.
$$(0.9 \pm 0.2)M_{2/n}O : Al_2O_3 : wSiO_2 : yH_2O$$

where "M" is at least one cation having a valence not more than 3, "n" represents the valence of "M", "w" is a value greater than 3 up to 8, and "y" is a value up to 9 depending upon the identity of "M", and the degree of hydration of the crystal.

The terms "type X zeolite" and "type Y zeolite" as employed herein refer not only to type X structured and type Y structured zeolites containing sodium cations as the cation "M" indicated in the formulas above but also refer to those containing other additional cations such as hydrogen cations, the alkali metal cations, or the alkaline earth cations. Typically both the type X and type Y structured zeolites as

initially prepared and as used as a base material for the special adsorbent described herein are predominantly in the sodium form but they usually contain any or all of the cations mentioned above as impurities. The term "exchanged cationic site" generally refers to the site in the zeolite occupied by the cation "M". This cation, usually sodium, can be replaced or exchanged with other specific cations, depending on the type of the zeolite to modify characteristics of the zeolite.

The precursor mass may be any type X or type Y zeolite-containing starting material used to make the special adsorbent described below. Generally the precursor mass will be in the form of particles such as extrudates, aggregates, tablets, pills, macrospheres, or granules produced by grinding any of the above to a desired size range. The type X or type Y zeolite can be present in the precursor mass in concentrations generally ranging from 75 wt.% to 98 wt.% of the precursor mass based on a volatile free composition. The remaining material in the precursor mass generally comprises amorphous silica or alumina or both which is present in intimate mixture with the zeolite material. This amorphous material may be an adjunct of the manufacturing process of the type X or type Y zeolite (for example, intentionally incomplete purification of the zeolite during its manufacture) or it may be added to the relatively pure zeolite to aid in forming or agglomerating particles of the zeolite.

One example of a precursor mass is commercially available nominal 1/15-inch extrudate comprising 13X zeolite and a minor amount of amorphous material as binder. This precursor mass is primarily in the sodium form; that is, the cation represented as "M" in formula 2 above is primarily sodium. By chemical analysis the Na_2O/Al_2O_3 ratio of this precursor mass is usually 0.7:1 or less and can typically be about 0.5:1. This, of course, is less than the $0.9\pm0.2:1$ indicated in formula 2 above. Other cations such as $H+$ and any of the Group IIA metal cations may be present, primarily as impurities, to supply the remainder of the cations needed for chemical balance and to meet the 0.9 ± 0.2 Na_2O/Al_2O_3 ratio. The silica to alumina ratio of this starting material by X-ray determination is about 2.5 and the same ratio by chemical analysis is about 2.6. Normally the precursor mass whether in the extrudate or pellet form is granulated to a particle size range of 20—40 mesh (Standard U.S. Mesh) before the first ion exchange step is begun. This is approximately the desired particle size of the finished adsorbent.

We have found that treating a type X or type Y precursor mass with a dilute aqueous sodium hydroxide solution prior to a subsequent ion exchange of the treated base material to effect the replacement of sodium cations at the exchangeable cationic sites with selected cations of one or more Group IA, IIA or IB metals produces a superior adsorbent when used in a process for the separation of an extract component from a feed mixture comprising an extract component and a raffinate component. This treatment step is in the nature of an ion exchange step (and will hereinafter be referred to as the first ion exchange) since the NaOH solution replaces non-sodium impurities in the type X or type Y zeolite contained in the precursor mass thereby converting the zeolite essentially completely to the sodium form. More specifically, to produce an acceptable adsorbent it is preferred that the sodium content of the starting material, as characterised by the weight ratio Na_2O/Al_2O_3, be increased to a ratio greater than 0.7:1 and more preferably from 0.75:1 to 1:1. The first ion exchange conditions are preferably so regulated to achieve this degree of ion exchange.

Increasing the sodium content of the precursor mass appears to permit a higher loading into the zeolite of one or more other selected cations during a second subsequent ion exchange thus producing, for reasons not fully understood, a superior adsorbent. It is these selected cations and the SiO_2/Al_2O_3 ratio of the zeolite which determines the adsorbent properties (hereinafter discussed in more detail) which make possible various adsorptive separation processes.

Although mild ion-exchange conditions are employed for this first ion exchange this step additionally removes a small amount of silica and alumina. Total silica and alumina removal from the precursor mass is usually from 1 to 15% and is generally in the range of 1 to 5 wt.%. Analyses indicate that the bulk of both soluble and insoluble material removed from the base material is aluminum as alumina or sodium aluminate. At least a portion of the alumina extracted appears to be from the zeolite itself rather than from any amorphous material since there is some nominal loss of zeolite as detected by X-ray analysis after this step. It is not known whether the small amount of silica removed from the precursor mass came from the crystalline (zeolite) portion or the amorphous portion of the base material.

The degree of ion exchange and extraction of alumina achieved is a function of the three variables of caustic concentration, temperature at which the ion exchange is conducted, and the length of time the ion exchange is continued.

The sodium hydroxide used to prepare the aqueous sodium hydroxide solution should be of high purity having very low levels of both other Group IA impurities and Group IIA impurities. Suitable concentrations to obtain the desired ion exchange can be from 0.5 to 10 wt.% of the sodium hydroxide with the preferred concentration being from 0.5 to 5 wt.%. By using solutions containing sodium hydroxide within these ranges of concentration, the desired ion exchange can be obtained at temperatures from 50 to 250°F. with temperatures from 150 to 250°F. being especially preferred. Operating pressure is not critical and need only be sufficient to ensure a liquid phase. Operating pressures can range from atmospheric pressure to 100 psig. The length of time required for the ion exchange will usually vary, depending upon the solution concentration and temperature, from 0.5 to 5 hours. Within the above preferred concentrations and temperature ranges, a contact time which has been shown to be especially preferred is 2 to 3 hours. Continuous or batch-type operations can be employed. The ion exchange step will be controlled so that the zeolite structure will not be destroyed. The final product will as a general rule have a Na_2O/Al_2O_3 ratio greater than 0.7:1 and more preferably from 0.75:1 to 1:1.

After the first ion-exchange step the sodium exchanged particles are treated at second ion-exchange conditions to effect the essentially complete exchange of the sodium cations at the exchangeable cationic sites in the zeolite with one or more other selected cations.

The cations which may be placed upon the zeolite are selected from one or more of the metals of Group IA, Group IIA, and Group IB of the Periodic Table of Elements, subject to the disclaimers hereinafter. In particular, adsorbents comprising type X zeolites containing cations of one or more metals selected from lithium, rubidium, cesium, beryllium, magnesium, calcium, strontium, copper and silver, with or without potassium and/or barium, or containing potassium cations, at the exchangeable cationic sites, and adsorbents comprising type Y zeolites containing cations of one or more metals selected from lithium, beryllium, magnesium, calcium, strontium, copper and silver, with or without potassium, rubidium, cesium and/or barium, at the exchangeable cationic sites, can be used in various separation processes for the separation of an extract component from a feed mixture comprising an extract component and a raffinate component.

Cationic or base exchange methods are generally known to those familiar with the field of crystalline aluminosilicate production. They are generally performed by contacting the zeolite with an aqueous solution of the soluble salts of the cation or cations desired to be placed upon the zeolite. The desired degree of exchange takes place and then the sieves are removed from the aqueous solution, washed, and dried to a desired water content. It is contemplated that cation exchange operations may take place using individual solutions of desired cations to be placed on the zeolite or using an exchange solution containing a mixture of cations, where two or more desired cations are to be placed on the zeolite.

When singular cations are base exchanged upon a zeolite the singular cations can comprise anywhere from 5 up to 75 wt.% on a relative volatile free basis of the zeolite depending upon the molecular weight of the material exchanged upon the zeolite. It is contemplated that when single ions are placed upon the zeolite that they may be on the zeolite in concentrations of from 1% to 100% of the original cations present (generally sodium) upon the zeolite prior to its being ion-exchanged. By knowing the empirical formula of the zeolite used, its water content and the percentage of any amorphous material or binder present if any, it is possible to calculate the percentage of ion exchange that has taken place.

When two or more different cations are placed upon the zeolite there is an additional parameter in which one can operate in order to effectively produce a zeolite having the desired properties. Besides the extent of the zeolite ion exchange, which is determined by variables such as the length of ion-exchange times, ion-exchange temperature, and cation concentrations, one can also vary the ratio of individual cations placed on the zeolite. In instances in which the cation pairs comprise a Group IIA metal and a Group IA metal the weight ratio of these two components upon the zeolite can vary anywhere from less than one up to two hundred depending upon the molecular weight of the Group IIA or Group IA metal.

Second ion-exchange conditions generally include a temperature of from 50°F. to 250°F. and a pH sufficient to preclude the formation of the hydrogen form of the zeolite. The pH is therefore usually greater than 7 and preferably within the range of 7 to 10. Operating pressure is not critical and need only be sufficient to insure a liquid phase. Operating pressures can range from atmospheric pressure to 150 psig. The length of time for the essentially complete exchange of the sodium

cations is generally from 0.5 to 5 hours depending upon the concentration of the cation in the ion exchange medium and the temperature. The term "essentially complete exchange" as used herein means that the sodium cation content of the base material has been reduced to 2.0 wt.% or less and more preferably to 1 wt.% or less.

When the adsorbent is to contain more than one cation at the exchangeable cationic sites it is preferred that the second ion exchange be done in more than one step, each step being an ion exchange with an aqueous solution containing a single cation. For example, if the adsorbent were to be required to contain both barium and potassium, the sodium exchanged particles, produced by the first ion exchange, could be ion exchanged first with an aqueous solution of a potassium salt, preferably an aqueous solution of potassium chloride, for a time sufficient to reduce the sodium cations to less than 2 wt.% of the zeolite and yield the potassium form of the zeolite. The exchange could be either a continuous or a batch type operation. The ion-exchange could suitably be accomplished on passing a 7 wt.% aqueous potassium chloride solution through a bed of the sodium-exchanged particles at about 180°F. at a liquid hourly space velocity of about one until a total of approximately 13 pounds of solution per pound of said particles had been passed in contact therewith. Small amounts of potassium hydroxide would usually be added to the ion exchange solution to maintain the pH of the solution within the range of from 7 to 10. Since the primary purpose of the sodium cation ion exchange was to remove hydrogen cation (and metal cation) contaminants, this pH range is necessary to avoid redepositing hydrogen cation on the adsorbent mass.

The potassium-exchanged particles could then be washed with water to remove excess ion-exchange solution. The washing medium would usually be water to which had been added small amounts of potassium hydroxide to adjust and maintain the pH within the range of 7 to 10. Washing temperatures could include temperatures within the range of 100°F. to 200°F. with a temperature of 100°F. to 145°F. preferred. Although the washing step could be done in a batch manner with one aliquot of wash water at a time, the washing step would generally and preferably be done on a continuous flow type basis with water passed through a bed of the adsorbent at a given liquid hourly space velocity and a temperature for a period of time in order that from 1 to 5 gallons of water per pound of starting material would be used to wash the material. Preferred washing conditions would include using liquid hourly space velocities from 0.5 to 5, with 1.5 being preferred, to pass from 1 to 5 gallons of wash water per pound of starting material over the ion exchanged adsorbent.

The potassium-exchanged particles would then be ion exchanged with an aqueous solution of a barium salt in the second step of the two-step ion-exchange procedure to achieve the desired weight ratio of barium to potassium on the finished adsorbent. Preferably an aqueous solution of from 0.2 to 5 wt.% barium chloride would be recycled through the particle bed at about 180°F. and at a liquid hourly space velocity of from 1 to 5 until the desired degree of exchange had been achieved. After the barium-exchange step had been completed, the water-washing step would be repeated, again maintaining a pH of 7 or greater in order to prevent the possibility of formation of the hydrogen form of the zeolite. A good indication of complete washing could be made by quantitatively testing the effluent wash water for the presence of the anion portion of the salt used in the ion exchange solution.

The order of the potassium and barium exchanges could also be reversed with the barium exchange first and the potassium exchange second. It would also be possible to employ a single step ion-exchange in which both barium and potassium were placed on the zeolite. The two-step procedure, however, allows more precise control of the amount of cations placed on the zeolite. Although this second ion exchange, whether conducted in one step or two, has been described above in terms of potassium and barium it does, of course, equally apply with other pairs of the cations previously described.

When it is desired that the sodium exchanged particles resulting from the first ion exchange be essentially completely exchanged with a single cation, such as potassium, then a procedure like that of the first step alone of the above described two-step procedure can be employed.

When the wash step is completed, the wet adsorbent particles will usually contain from about 30 to about 50 wt.% volatile matter (water) as measured by loss on ignition to 900°C. In this specification, the volatile matter content of the zeolitic adsorbent is determined by the weight difference obtained before and after drying a sample of adsorbent in a high temperature furnace at 900°C. under an inert purge gas stream such as nitrogen for a period of time sufficient to achieve a constant weight. The difference in weight, calculated as a percentage of the sample's initial weight,

is reported as loss on ignition (LOI) at 900°C. and represents the volatile matter present within the adsorbent.

The remaining step in the method of manufacture then is the drying step to reduce the LOI at 900°C. to less than 10 wt.% with the preferred LOI being 3 to 7 wt.%. After the washing has been completed, the particles can be unloaded and dried in a forced-air oven at temperatures above the boiling point of water but less than 500°C. and preferably 150°C., for a period of time sufficient to remove enough water so that the volatile matter content of the zeolite is below 10 wt.%. Other methods of drying may be used which can include drying in the presence of an inert gas or under a vacuum or both.

The feed component more selectively adsorbed on the adsorbent is commonly referred to as the extract component of the feed mixture, while the less selectively adsorbed component is referred to as the raffinate component. To separate the extract component from a feed mixture containing an extract component and a raffinate component the mixture is contacted with the adsorbent and the extract component is more selectively adsorbed and retained by the adsorbent while the raffinate component is relatively unadsorbed and is removed from the interstitial void spaces between the particles of adsorbent and the surface of the adsorbent. The adsorbent containing the more selectively adsorbed extract component is referred as a "rich" adsorbent-rich in the more selectively adsorbed extract component. The extract component is thereafter removed from the adsorbent by methods hereinafter described. Fluid streams leaving the adsorbent comprising an extract component and comprising a raffinate component are referred to, respectively, as the extract stream and the raffinate stream.

Although it is possible by the process of this invention to produce high purity (98% or greater) extract component product at high recoveries, it will be appreciated that an extract component is never completely adsorbed by the adsorbent, nor is a raffinate component completely non-adsorbed by the adsorbent. Therefore, small amounts of a raffinate component can appear in the extract stream, and, likewise, small amounts of an extract component can appear in the raffinate stream. The extract and raffinate streams then are further distinguished from each other and from the feed mixture by the ratio of the concentration of an extract component and a specific raffinate component, both appearing in the particular stream. As one specific example, when the adsorbent is used to separate aromatic hydrocarbon isomers, the ratio of the concentration of the more selectively adsorbed para-isomer to the concentration of the less selectively adsorbed meta-isomer will be highest in the extract stream, next highest in the feed mixture, and lowest in the raffinate stream. Likewise, the ratio of the less selectively adsorbed meta-isomer to the more selectively adsorbed para-isomer will be highest in the raffinate stream, next highest in the feed mixture, and the lowest in the extract stream.

The adsorbent can be contained in one or more chambers where through programmed flow into and out of the chambers separation of the extract component is effected. The adsorbent will preferably be contacted with a desorbent material which is capable of displacing the extract component from the adsorbent. An extract stream comprising the extract component and desorbent material will then be withdrawn from the adsorbent and the desorbent material separated thereby leaving high purity extract component. Alternatively, the extract component could be removed from the adsorbent by purging or by increasing the temperature of the adsorbent or by decreasing the pressure of the chamber or vessel containing the adsorbent or by a combination of these means.

The adsorbent may be employed in the form of a dense compact fixed bed which is alternatively contacted with the feed mixture and a desorbent material (hereinafter described in more detail). In the simplest embodiment of the invention the adsorbent is employed in the form of a single static bed in which case the process is only semi-continuous. A set of two or more static beds may be employed in fixed-bed contacting with appropriate valving so that the feed mixture is passed through one or more adsorbent beds while the desorbent material is passed through one or more of the other beds in the set. The flow of feed mixture and desorbent material may be either up or down through the desorbent. Any of the conventional apparatus employed in static bed fluid-solid contacting may be used. Countercurrent moving-bed or simulated countercurrent moving-bed liquid flow systems, however, have a much greater separation efficiency than fixed adsorbent bed systems and are therefore preferred. In the moving-bed or simulated moving-bed processes the adsorption and desorption operations are continuously taking place which allows both continuous production of an extract and a raffinate stream and the continual use of feed and

desorbent streams. One preferred processing flow scheme which can be utilized to effect the process of this invention includes what is known in the art as the simulated moving-bed countercurrent system. The general operating sequence of such a flow system is described in U.S. Patent 2,985,589 issued to D. B. Broughton, and more specifically in U.S. Patents 3,556,589; 3,556,732; 3,626,020; 3,683,638; and 3,686,342. These patents describe the processing sequence of the 2,985,589 patent employed in particular simulated moving-bed counter-current solid-fluid contacting processes. The processing sequence disclosed in these patents is the preferred mode of operating the separation process disclosed herein.

One broad embodiment of the process to use the adsorbent produced by the method of this invention is a process for separating an extract component from a feed mixture containing an extract component and a raffinate component which process generally employs the operating sequence described in U.S. Patent 2,985,589 and which comprises the steps of: contacting the feed mixture with the specially prepared adsorbent at adsorption conditions to effect the selective adsorption of the extract component from the feed mixture, withdrawing from the bed of adsorbent a raffinate stream, contacting the adsorbent with a desorbent material at desorption conditions to effect desorption of the extract component from the adsorbent; and, withdrawing an extract stream from the adsorbent.

Adsorption and desorption conditions for adsorptive separation processes can generally be either in the liquid or vapor phase or both but for aromatic isomer separation processes employing zeolitic adsorbents all liquid-phase operations are usually preferred because of the lower temperature requirements and the slightly improved selectivities associated with the lower temperatures. Preferred adsorption conditions for the process of this invention will include temperature within the range of from 100°F. to 450°F. and will include pressures in the range from atmospheric to 500 psig. Pressures higher than 500 psig. do not appear to affect the selectivity to a measureable amount and additionally would increase the cost of the process. Desorption conditions for the process of the invention shall generally include the same range of temperatures and pressures as described for adsorption operations. The desorption of the selectively adsorbed isomer could also be effected at subatmospheric pressures or elevated temperatures or both or by vacuum purging of the adsorbent to remove the adsorbed isomer but this process is not directed to these desorption methods.

The desorbent materials which can be used in the various processing schemes employing this adsorbent will vary depending on the type of operation employed. The term "desorbent material" as used herein shall mean any fluid substance capable of removing a selectively adsorbed feed component from the adsorbent. In the swing-bed system in which the selectively adsorbed feed component is removed from the adsorbent by a purge stream desorbent materials comprising gaseous hydrocarbons such as methane, ethane, etc., or other types of gases such as nitrogen or hydrogen may be used at elevated temperatures or reduced pressures or both to effectively purge the adsorbed feed component from the adsorbent.

However, in adsorptive separation processes which employ zeolitic adsorbents and processes which are generally operated at substantially constant pressures and temperatures to insure liquid phase, the desorbent material relied upon must be judiciously selected to satisfy several criteria. First, the desorbent material must displace the adsorbed feed component from the adsorbent with reasonable mass flow rates without itself being so strongly adsorbed as to unduly prevent the extract component from displacing the desorbent material in a following adsorption cycle. Secondly, desorbent materials must be compatable with the particular adsorbent and the particular feed mixture. More specifically, they must not reduce or destroy the critical selectivity of the adsorbent for the extract component with respect to the raffinate components.

Desorbent material should additionally be substances which are easily separable from the feed mixture that is passed into the process. In desorbing the preferentially adsorbed component of the feed, both desorbent material and the extract component are removed in admixture from the adsorbent. Without a method of separation such as distillation of these two materials, the purity of the extract component of the feed stock would not be very high since it would be diluted with desorbent. It is therefore contemplated that desorbent materials used in processes employing adsorbents prepared by this method will have a substantially different average boiling point than that of the feed mixture. The use of a desorbent material having a substantially different average boiling point than that of the feed allows separation of desorbent material from feed components in the extract and raffinate streams by simple fractionation thereby permitting reuse of desorbent material in the process. The term "substantially

different" as used herein shall mean that the difference betwen the average boiling points between the desorbent material and the feed mixture shall be at least 15°F. The boiling range of the desorbent material may be higher or lower than that of the feed mixture.

One particular process which can employ adsorbents prepared by the method of my invention is a process for the separation of fructose from glucose in a mixture thereof. The preformed adsorbent material for such process is a calcium exchanged Y zeolite and a suitable desorbent is water. Another adsorption process is one for the separation of the paraisomer from a hydrocarbon feed mixture comprising at least two bi-alkyl substituted aromatic isomers, including the paraisomer, the isomers having from 8 to 18 carbon atoms per molecule.

Feed mixtures to this process will contain alkyl substituted monocyclic hydrocarbon isomers characterised by Formula 3 below:

Formula 3.
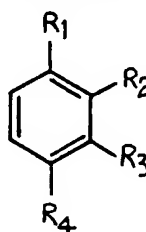
wherein R_1, R_2, R_3, and R_4 are alkyl chains in a manner to allow an essentially bi-alkyl substitution at either ortho-, meta-, or para-isomer positions. The R substitutional groups can include alkyl groups ranging from methyl substitution groups up to and including chains having 11 or less carbon atoms per molecule. The alkyl side chains can be both normal and branched in nature and are preferably saturated chains.

Specific representative compounds which can be utilised as feedstocks in this particular process include those feedstocks containing the xylene isomers and ethylbenzene and the various isomers of methylethylbenzene, diethylbenzene, isopropyltoluene (cymene), the methylpropylbenzenes, ethylpropylbenzenes, methylbutylbenzenes, ethylbutylbenzene, dipropylbenzenes, methylpentylbenzene, and combinations thereof. The above list only represents a small fraction of compounds whose isomers can be separated in an adsorptive-separation process which employs the specially prepared adsorbent produced by the method of this invention. Thus this process will be typically used to separate para-xylene from a feed mixture comprising para-xylene and at least one other C_8 aromatic isomer; para-diethylbenzene from a feed mixture comprising para-diethylbenzene and at least one other diethylbenzene isomer, and para-cymene from a feed mixture comprising para-cymene and at least one other cymene isomer to name a few.

The isomers of such compounds are separated by the adsorbent in this process according to their configuration depending whether they are of a para-, meta-, or ortho-isomer construction. Specifically, the para-isomer is selectively adsorbed relative to the other isomers. It is contemplated that with feed stocks containing mixtures of more than one class of isomers (for example, C_8 isomers in mixture with C_9 or C_{10} isomers) molecular weight differences will unduly interfere with selective adsorption based upon isomer configuration differences. It is therefore preferred that this process employ feed stocks comprising only a single class of aromatic isomers, that is, aromatic isomers having an equal number of carbon atoms per molecule. It is more preferable to use isomers having as their only differences the location of the alkyl substituted groups in a para-, meta-, or ortho-position. The alkyl structures should preferably be the same for each isomer of a class. In some instances an isomer may have alkyl chains which are both normal or branched or one branched and one normal.

The feed stocks may contain small quatities of straight or branched chain paraffins, cycloparaffins or olefinic material. It is preferable to have these quantities at a minimum amount in order to prevent contamination of products from this process by materials which are not selectively adsorbed or separated by the adsorbent. Preferably, the above-mentioned contaminants should be less than about 20% of the volume feed stock passed into the process.

Preferred desorbent materials for use in this process are those comprising toluene

and diethylbenzene. Mixtures of these compounds with paraffins are also effective as desorbent materials. Such paraffins must be compatable with the particular adsorbent and feed mixture as described above and must be easily separable from the feed mixture. The paraffins can include straight or branched chain paraffins or cycloparaffins which meet these criteria. Typical concentrations of toluene or diethylbenzene in mixtures of same and a paraffin can be from a few volume percent up to near 100 vol.% of the total desorbent material mixture but such concentrations preferably will be within the range of from about 50 vol.% to about 100 vol.% of the mixture.

The improved adsorbent produced by the method of the invention can be better understood by brief reference to certain adsorbent properties which are necessary to the successful operation of a selective adsorption process. It will be recognized that improvements in any of these adsorbent characteristics will result in an improved separation process. Among such characteristics are: adsorptive capacity for some volume of an extract component per volume of adsorbent; the selective adsorption of an extract component with respect to a raffinate component and the desorbent material; sufficiently fast rates of adsorption and desorption of the extract component to and from the adsorbent; and, in instances where the components of the feed mixture are very reactive, little or no catalytic activity for undesired reactions such as polymerisation and isomerisation.

Capacity of the adsorbent for adsorbing a specific volume of an extract component, is of course, a necessity; without such capacity the adsorbent is useless for adsorptive separation. Furthermore, the higher the adsorbent's capacity for an extract component, the better is the adsorbent. Increased capacity of a particular adsorbent makes it possible to reduce the amount of adsorbent needed to separate the extract component contained in a particular charge rate of feed mixture. A reduction in the amount of adsorbent required for a specific adsorptive separation reduces the cost of the separation process. It is important that the good initial capacity of the adsorbent be maintained during actual use in the separation process over some economically desirable life.

The second necessary adsorbent characteristic is the ability of the adsorbent to separate components of the feed; or, in other words, that the adsorbent possess adsorptive selectivity for one component as compared to another component. Some adsorbents demonstrate acceptable capacity but possess little or no selectivity. Relative selectivity can be expressed not only for one feed mixture component as compared to another but can also be expressed between any feed mixture component and the desorbent. The relative selectivity, (B), as used throughout this specification is defined as the ratio of two components of an adsorbed phase over the ratio of the same two components in an unadsorbed phase at equilibrium conditions.

Relative selectivity is shown as Equation 1 below:

Equation 1.

$$\text{Selectivity} = (B) = \frac{[\text{vol.percent C/vol.percent D}]\ A}{[\text{vol.percent C/vol.percent C}]\ U}$$

where C and D are two components of the feed represented in volume percent and the subscripts A and U represent the adsorbed and unadsorbed phases respectively. The equilibrium conditions were determined when the feed passing over a bed of adsorbent did not change composition after contacting the bed of adsorbent. In other words, there was no net transfer of material occurring between the unadsorbed and adsorbed phases.

Where selectivity of two components approaches 1.0 there is no preferential adsorption of one component by the adsorbent with respect to the other, they are both adsorbed (or non-adsorbed) to about the same degree with respect to each other. As the (B) becomes less than or greater than 1.0 there is a preferential adsorption by the adsorbent for one component with respect to the other. When comparing the selectivity by the adsorbent of one component C over component D, a (B) larger than 1.0 indicates preferential adsorption of component C within the adsorbent. A (B) less than 1.0 would indicate that component D is preferentially adsorbed leaving an unadsorbed phase richer in component C and an adsorbed phase richer in component D. Desorbent materials ideally would have a selectivity equal to about 1 or slightly less than 1 with respect to an extract component.

The third important characteristic is the rate of exchange of the extract com-

ponent of the feed mixture material or, in other words, the relative rate of desorption of the extract component. This characteristic relates directly to the amount of desorbent material that must be employed in the process to recover the extract component from the adsorbent, faster rates of exchange reduce the amount of desorbent material needed to remove the extract component and therefore permit a reduction in the operating cost of the process. With faster rates of exchange, less desorbent material has to be pumped through the process and separated from the extract stream for reuse in the process.

The adsorbents produced by the method of this invention not only have good capacity and good selectivity but have faster transfer rates than do any adsorbents not produced by this method.

It is also necessary that the adsorbent possess little or no catalytic activity toward any reaction such as polymerisation of isomerisation of any of the feed components. Such activity might effect adsorbent capacity or selectivity or product yields or all of these. Where the feed mixture contains relatively stable components, such as the aromatic hydrocarbon isomers, this is generally not a problem. However, when the feed mixture contains very reactive components, such as the pinene isomers or butadiene, this adsorbent property is of considerable importance.

In order to test various adsorbents and desorbent materials with a particular feed mixture to measure the adsorbent characteristics of adsorptive capacity and selectivity and exchange rate a dynamic testing apparatus has been employed. The apparatus consists of an adsorbent chamber of approximately 70 cc volume having inlet and outlet portions at opposite ends of the chamber. The chamber is contained within a temperature control means and, in addition, pressure control equipment is used to operate the chamber at a constant predetermined pressure. Chromatographic analysis equipment can be attached to the outlet line of the chamber and used to analyse the effluent stream leaving the adsorbent chamber.

A pulse test, performed using this apparatus and the following general procedure, is used to determine selectivities and other data for various adsorbent systems. The adsorbent is filled to equilibrium with a particular desorbent material by passing the desorbent material through the adsorbent chamber. At a convenient time, a pulse of feed containing known concentrations of a non-adsorbed tracer and of an extract and raffinate component all diluted in desorbent material is injected for a duration of several minutes. Desorbent flow is resumed, and the tracer and the extract and raffinate components are eluted as in a liquid-solid chromatographic operation. The effluent is analysed by on-stream chromatographic equipment and traces of the envelopes of corresponding component peaks are developed.

From information derived from the chromatographic traces adsorbent performance can be rated in terms of capacity index for the extract component, selectivity for the extract component with respect to the raffinate component, and rate of desorption of the extract component by the desorbent material. The capacity index is characterised by the distance between the center of the extract component peak envelope and the tracer peak envelope and is expressed in terms of the volume in cubic centimeters of desorbent pumped during this time interval. Selectivity, (B), for the extract component with respect to the raffinate component is characterised by the ratio of the distance between the center of the extract component peak envelope and the tracer peak envelope to the corresponding distance for the raffinate component. The transfer rates are, we have found, best characterised by the width of the tracer peak envelope at half intensity. The narrower the peak width, the faster the desorption rate.

To further evaluate promising adsorbent systems and to translate this type of data into a practical separation process requires actual testing of the best system in a continuous countercurrent liquid-solid contacting device.

The general operating principles of such a device have been previously described and are found in Broughton U.S. Patent 2,985,589 and a specific laboratory-size apparatus utilising these principles is described in deRosset et al U.S. Patent 3,700,812. The equipment comprises multiple adsorbent beds with a number of access lines attached to distributors within the beds and terminating at a rotary distributing valve. At a given valve position, feed and desorbent are being introduced through two of the lines and raffinate and extract are withdrawn through two more. All remaining access lines are inactive and when the position of the distributing valve is advanced by one index, all active positions will be advanced by one bed. This simulates a condition in which the adsorbent physically moves in a direction countercurrent to the liquid flow. Additional details on adsorbent testing and evaluation may be found in the paper "Separation of C_8 Aromatics by Adsorption" by A. J.

deRosset, R. W. Neuzil, A. J. Korous, and B. H. Rosback presented at the American Chemical Society, Los Angeles, California, March 28 — April 2, 1971.

The superior performance of these specially prepared adsorbents which was indicated by the pulse test results was confirmed by continuous testing in this device.

The examples shown below are intended to further illustrate the method of this invention and adsorbents produced thereby. The examples present pulse test results for various adsorbents produced by the method of the invention.

EXAMPLE I.

This example presents retention volume and selectivity results obtained from pulse tests of ketose-aldose mixtures with seven X zeolite adsorbents. The specific crystalline aluminosilicate adsorbents of this example (apart from the control adsorbent which is merely Na-exchanged) were prepared by the method of this invention.

Nominal 1/16-inch extrudate containing Linde type 13X zeolite (LINDE is a Registered Trade Mark) was ground to produce 16—40 U.S. Standard Mesh particle size material having chemical and physical properties as shown in Table 1 below:

TABLE NO. 1.
Properties of the Starting Material.

Chemical Properties

Volatile Matter (loss on ignition @ 900°C), wt.%	3.2
SiO_2 (volatile free) wt.%	50.7
Al_2O_3 (volatile free) wt.%	33.6
Na_2O (volatile free) wt.%	12.4
Na_2O/Al_2O_3	.61
SiO_2/Al_2O_3	2.56

Physical Properties

Apparent Bulk Density, gm/cc	0.635
Surface Area, m²/gm	500
Pore Volume, ml/gm	0.30
Pore Diameter, A	24
Area % faujasite (X-ray)	93
SiO_2/Al_2O_3 (X-ray)	2.5

One hundred pounds of the granular starting material was loaded into an ion exchange tower against an upward flow of 1.6 wt.% NaOH solution at a rate such that the effluent temperature did not exceed 145_2°F. After all of the material was loaded, the material was ion exchanged by passing the 1.6 wt.% NaOH solution upflow through the ion exchange tower at a liquid hourly space velocity of 1.5 and a temperature of 200°F. until a total of 0.335 pounds of NaOH per pound of volatile-free starting material had been passed through the tower. After this first ion exchange the material was water-washed to remove excess NaOH solution by passing treated water, having a pH of 9, upflow through the tower at 1.5 LHSV and 140°F. to a total of 1.3 gallons of water per pound of volatile-free starting material. Test samples of particles removed after this wash had the properties as shown in Table 2 below: —

TABLE NO. 2.
Properties of the Sodium-exchanged Material.

Chemical Properties

Volatile Matter (loss on ignition @ 900°C), wt.%	25.4
SiO_3 (volatile free) wt.%	48.0
Al_2O_3 (volatile free) wt.%	32.1
Na_2O (volatile free) wt.%	15.3
Na_2O/Al_2O_3	0.81
SiO_2/Al_2O_3	2.54

Physical Properties

Apparent Bulk Density, gm/cc	0.671
Surface Area, m²/gm	516
Pore Volume, ml/gm	0.27
Pore Diameter, A	21
Area % faujasite (X-ray)	110
SiO_2/Al_2O_3 (X-ray)	2.5

1,589,213

The second ion-exchange conditions were then effected separately to produce essentially completely exchanged X zeolites with the cations of metals K, Cs, Mg, Ca, Sr and Ba+Sr by the one and two-step procedure previously described (Na−X = unexchanged 13X sieves for a control test).

The ion exchanged and washed materials were then dewatered, unloaded from the ion exchange tower, and dried in a forced air oven at 570°F. to a volatile content of about 2.0 wt.%

The general pulse-test apparatus and procedure have been previously described. The adsorbents were tested in a 70 cc coiled column maintained at 55°C. and 4.4 atmospheres absolute pressure, and using pure water as the desorbent material. The sequence of operations for each test was as follows: Desorbent material (water) was continuously run through the column containing the adsorbent at a nominal liquid hourly space velocity (LHSV) of about 1.0. At a convenient time desorbent flow was stopped, a 4.7 cc sample of 10 wt.% fructose in water was injected into the column via a sample loop, and the desorbent flow was resumed. The emergent sugar was detected by means of a continuous refractometer detector and a peak envelope trace was developed. Another pulse containing 10 wt.% glucose was similarly run. A saturated water solution of benzene was also injected to serve as a tracer from which the void volume of the adsorbent bed could be determined. Thus, for each adsorbent tested, three peak traces were developed, one for glucose, one for fructose and one for benzene. The retention volume for glucose is calculated by measuring the distance from time zero or the reference point to the midpoint of the glucose peak and subtracting the distance representing the void volume of the adsorbent obtained by measuring the distance from the same reference point to the mid-point of the benzene peak. For some adsorbents both the fructose and glucose peaks were essentially on top of the benzene peak envelope indicating that both monosaccharides were relatively unadsorbed by the particular adsorbents in the presence of water. The selectivity of an adsorbent for fructose with respect to glucose is the quotient obtained by dividing the fructose retention volume by the glucose retention volume. The results for these tests are shown in Table No. 3 below.

TABLE 3

Selectivities of Various Adsorbents for Fructose with Respect to Glucose

Test	Adsorbent	Retention Vol. of Fructose, cc.	Retention Vol. of Glucose, cc.	Selectivity (B)
1	Na−X	7.1	5.0	1.42
2	K−X	11.9	21.6	0.55
3	Cs−X	Both were relatively unadsorbed		
4	Mg−X	Both were relatively unadsorbed		
5	Ca−X	Both were relatively unadsorbed		
6	Sr−X	8.0	1.3	6.15
7	Ba−Sr−X	21.3	4.2	5.0

The adsorbents used for tests 1 through 3 were three X zeolites each containing at the exchangeable cationic sites cations of metals from Group IA of the Periodic Table of Elements. The K—X adsorbent used for test 2 had a "selectivity" of 0.55 (for fructose with respect to glucose), and therefore actually exhibited selectivity for glucose with respect to fructose. The Na-X adsorbent used for test 1 (selectivity of 1.42) exhibited selectivity for fructose with respect to glucose, while the Cs-X adsorbent used in Test 3 exhibited relative selectivity for neither. A K—Y adsorbent produced in a similar manner from Linde type SK—40 zeolite had a selectivity of 2.21.

The adsorbents used for Tests 4, 5 and 6 were X zeolites containing at exchangeable cationic sites cations of metals from Group IIA of the Periodic Table of Elements. Both fructose and glucose were relatively unadsorbed with the Mg-X and Ca-X adsorbents used in the presence of water for Tests 4 and 5, respectively, but the Sr-X adsorbent used in Test 6 exhibited selectivity for fructose with respect to glucose. A Ba-X adsorbent prepared in the same way had a selectivity of 2.82. While not definitely established, it is believed that adsorbents comprising X zeolites containing at the exchangeable cationic sites a Group IIA cation generally become less acidic as one moves downward from Period 3 to Period 6 of the Periodic Table of Elements in selecting the Group IIA cation. Thus, adsorbents comprising Ca- or Mg-exchanged X zeolites are unsuitable for use in the separation of glucose and fructose because they are more acidic, while adsorbents comprising a Sr-exchanged X zeolite are suitable for use in the separation of glucose and fructose because less acidic. Adsorbents comprising a Ba-exchanged X zeolite would also be suitable.

The adsorbent used for Test 7 was an X zeolite containing at exchangeable cationic sites the cation pair Ba and Sr. The Ba-Sr-X adsorbent used in Test 7 exhibited fructose-to-glucose selectivity less than the Sr-X adsorbent used in Test 5 but higher than a corresponding Ba-X adsorbent.

EXAMPLE II.

This example illustrates the ability of adsorbents manufactured by the method of the instant invention to separate a ketose from an aldose when operated in a preferred embodiment which utilizes a continuous, simulated-moving bed, counter-current-flow processing system. Specifically, the example presents test results obtained when a synthetic blend of fructose and glucose and some higher saccharides in water was processed using a Ca-Y adsorbent prepared by the method of this invention and water as a desorbent material in a pilot-plant-scale testing apparatus (described in U.S. Patent 3,706,816).

The raffinate and extract output streams were collected and analyzed for fructose and glucose concentrations by chromatographic analysis, but no attempt was made to remove the dionized water desorbent material deionized H_2O from them. Fructose yield was determined by calculating the amount of fructose "lost" to the raffinate stream, determining this quantity as a percentage of the fructose fed to the unit over a known period of time and subtracting this percentage from 100 percent.

The feed was processed as a 50% sugar solution in water. The solids content of the feed was 52% glucose, 42% fructose and 6% higher saccharides. The operating temperature was 60°C. The fructose purities (as a percent of total sugars present) of the extract output stream, and the fructose yields, are shown below in Table 4. (Pressure used was 10.5 atms. gauge)

TABLE 4

Test	Extract Stream Fructose Purity, %	Fructose Yield, %
1	97	10
2	94	49
3	92	65
4	87	83
5	84	88
6	80	90

By way of illustration, analysis of the extract and the raffinate streams at one point on the fructose purity-yield curve, 85% fructose yield point, were as shown in Table 5 below.

TABLE 5

Extract and Raffinate Stream Analysis at the 85% Yield Point

	Extract Stream	Raffinate Stream
% Fructose	88.3	10.7
% Glucose	11.7	79.5
% Higher Saccharides	Trace	9.8
% Sugars	14.9	13.3

The Ca-Y zeolite adsorbent, then, is an effective adsorbent for the relative separation of the fructose and glucose fractions.

EXAMPLE III.

This example illustrates the ability of adsorbents manufactured by the method of the instant invention when utilized in a continuously simulated moving bed counter-current type of operation to separate ethylbenzene in high purity at high recovery from a feed containing ethylbenzene at a concentration equal to or less than that of para-xylene.

The example presents test results obtained with Ca-X, Sr-X, and Sr-K-X adsorbents manufactured by the method of the instant invention in a pilot plant scale testing apparatus known as a carousel unit described in detail in U.S. Patent 3,706,816. Briefly, the apparatus consists essentially of 24 serially connected adsorbent chambers having about 44 cc volume each. Total chamber volume of the apparatus is approximately 1,056 cc. Operating temperature and pressure during the tests were 150°C and 11 atmospheres, respectively. The desorbent material used was toluene. Four feed materials were used, two of them having ethylbenzene concentrations considerably higher than the para-xylene concentrations and two of them having ethylbenzene concentrations about the same or less than the para-xylene concentrations. The analyses of the feed materials used are shown in Table 10 below.

The adsorbent comprising Ca-type X zeolite was Linde 10X Molecular Sieves of approximately 20—40 U.S. Mesh particle size range manufactured by the method of the instant invention. (LINDE is a Registered Trade Mark). Specifically, the adsorbent comprising Sr-type X zeolite was prepared from Linde 13X Molecular Sieves in the following manner. A 2.1 litre sample of Linde 13X Molecular Sieves in approximately 20—40 U.S. Mesh particle size range was loaded into an ion exchange tower against an upward flow of 1.6 wt.% NaOH solution at a rate such that the effluent temperature did not exceed 145°F. After all of the material was loaded, the material was ion exchanged by passing the 1.6 wt.% NaOH solution upflow through the ion exchange tower at a liquid hourly space velocity of 1.5 and a temperature of 200°F. until a total of 0.335 pounds of NaOH per pound of volatile-free starting material had been passed through the tower. Subsequently, the material was washed with 5 litres water at 60°C. The ion exchange was made by pumping 62 litres of 0.075 M Sr^{++} upflow at 1.3 litres/hour and 60°C. The void volumes were flushed downflow with 2 litres of deionized water at 25°C followed by upflow washing for 2 hours at 2 litre/hour and 45°C. After surface drying the exchanged material the adsorbent was further dried in a muffle furnace starting at 25°C and increasing the 500°C in 1/2 hour. The drying was continued at 500°C for 1/2 hour. The adsorbent analyzed 40.85 wt.% SiO_2, 29.74 wt.% Al_2O_3, 0.98 wt.% Na_2O, and 25.8 wt.% SrO. Based upon the alumina analysis, the adsorbent was 90.8 mole % exchanged. The adsorbent comprising Sr-K type X zeolite was prepared from Linde 13X Molecular Sieves in the following manner. A 1.0 litre sample of the Sr-exchanged material which was prepared in accordance with the method described above was ion exchanged with potassium by recycling 5 litres of 0.248 M K^+ solution at a flow rate of 2 litres per hour over the sample at 50°C for 40 hours. The void volumes were flushed downflow with 2 litres of 25°C deionized water followed by upflow washing with 2 litres deionized water in 1 hour and another 2 litres in 2 hours all at 60°C. After surface drying the exchanged material, the

adsorbent was further dried in a muffle furnace starting at 25°C and increasing
to 500°C in 1/2 hour. The drying was continued at 500°C for 1/2 hour. The
adsorbent analyzed 42.63 wt.% SiO_2, 29.16 wt.% Al_2O_3, 1.04 wt.% Na_2O, and
21.10 wt.% SrO, and 4.40 wt.% K_2O. Based upon the alumina analysis, the adsorbent
was 91.8 mole % exchanged. The apparatus was loaded first with the Ca-X adsorbent
and then the Sr-X adsorbent and then the Sr-K-X adsorbent. After each loading,
the adsorbents were then dried for 20 hours with 2.5 gm mol/hr of vapour phase
toluene at 150°C and atmospheric pressure. After the drying the adsorbent was re-
hydrated to known water contents by passing wet nitrogen from a water bubbler
over the adsorbent beds.

Two tests with each adsorbent were run, one with a feed having a relatively
high concentration of ethylbenzene with respect to para-xylene and the other with
a relatively low ethylbenzene concentration. The six tests, run at continuous steady-
state conditions, were performed to determine the ethylbenzene purity and recovery
relationships obtainable with feed material having relatively high and low ethylbenzene
concentrations. "Recovery" is determined by calculating the amount of ethylbenzene
which is lost through the extract stream, determining this quantity as a percentage of
the ethylbenzene fed into the process and subtracting this percentage from 100 percent.
Recovery then presents the percentage of ethylbenzene fed to the process which is not
lost to the extract stream. Distribution of the C_8 aromatics in the feed, extract and
raffinate was determined by gas chromatography. The test results are shown in Table
10 below.

TABLE 10
Carousel Test Results

Test	1	2	3	4	5	6
Adsorbent	Ca—X	Ca—X	Sr—X	Sr—X	Sr—K—X	Sr—K—X
Feed						
Distribution of C_8 Aromatics						
e, vol. %	32.0	20.0	29.2	17.0	21.6	19.3
p, vol. %	14.3	20.5	18.0	20.9	16.8	19.7
m, vol. %	33.3	44.2	39.8	47.4	47.2	46.0
o, vol. %	20.4	15.3	13.0	14.7	14.4	15.0
Extract Stream						
Distribution of C_8 Aromatics						
e, vol. %	2.8	12.4	0.7	0.1	0.1	0.3
p, vol. %	19.7	22.2	23.0	22.1	28.2	26.3
m, vol. %	48.1	49.9	59.3	60.8	52.2	64.9
o, vol. %	29.4	15.5	17.0	17.0	19.5	20.5
Raffinate Stream						
Distribution of C_8 Aromatics						
e, vol. %	98.2	98.7	98.2	97.5	99.2	99.7
p, vol. %	Tr	0.4	0.6	0.2	0.2	Tr
m, vol. %	0.3	0.8	0.8	2.1	0.4	0.3
o, vol. %	1.5	0.1	0.4	0.2	0.2	Tr
Recovery of Ethylbenzene in Raffinate %	98.6	34.1	98.0	99.0	99.0	99.0

In test 1 ethylbenzene was separated at high purity (98.2 vol.%) and at high recovery (98.6%). The deleterious effect of the strongly held toluene desorbent material has in this test been essentially eliminated because ethylbenzene is at a high enough concentration in the feed. The loss of ethylbenzene into the extract is shown by the results of test 2 where a feed containing an ethylbenzene concentration less than that of para-xylene was used. Although the purity was high (98.7 vol.%), the recovery was very low, 34.1%. For tests 3 and 4 with the Sr-X adsorbent and tests 5 and 6 with the Sr-K-X adsorbent on the other hand, ethylbenzene was separated at both high purity and at high recovery for feeds containing both high and low concentrations of ethylbenzene.

Our copending GB Patent Application No. 6540/76 (Serial No. 1,535,232) claims a method for preparing an adsorbent which comprises the steps of:— (a) contacting a base material comprising Y zeolite with an aqueous sodium hydroxide solution at first ion exchange conditions to effect the addition of sodium cations to said base material; (b) treating the sodium-exchanged base material at second ion exchange conditions to effect essentially complete exchange of the sodium cations with one or more cations selected from potassium, cesium and rubidium, such that the sodium cation content is reduced to 2.0 wt.% or less; and (c) drying the so-exchanged material to reduce the LOI (loss on ignition) at 900°C to less than 10 weight percent. It also claims an adsorbent prepared by such a method. We make no claim herein to such a method or to the adsorbent produced thereby.

We also make no claim herein to a method of manufacturing a solid adsorbent which comprises the steps of:—

(a) contacting a precursor mass containing type X or type Y zeolite and amorphous material with an aqueous sodium hydroxide solution at first ion exchange conditions to effect the addition of sodium cations to the zeolite structure;

(b) treating the sodium-exchanged mass at second ion exchange conditions to effect essentially complete exchange of sodium cations with barium or barium and potassium cations; and

(c) drying the resulting exchanged mass at conditions to reduce the loss on ignition at 900°C to less than 10 wt.%, nor to an adsorbent produced by such a method, bearing in mind that such a method and adsorbent are disclosed and claimed in our copending GB Patent Application No. 19016/74 (Serial No. 1,466,577).

Subject to these disclaimers,

WHAT WE CLAIM IS:—

1. A method of manufacturing a solid adsorbent which method comprises the steps of:

(a) contacting a precursor mass comprising X or Y zeolite with an aqueous sodium hydroxide solution at first ion exchange conditions to effect the addition of sodium cations to the zeolite structure;

(b) treating the sodium-exchanged mass at second ion exchange conditions to effect the essentially complete exchange of sodium cations with cations of one or more metals selected from Group IA, Group IIA, and Group IB of the Periodic Table of Elements; and

(c) drying the material at conditions to reduce the LOI at 900°C to less than 10 weight percent.

2. A method as claimed in claim 1 wherein the precursor mass initially has a Na_2O/Al_2O_3 ratio of less than 0.7:1.

3. A method as claimed in claim 1 or 2 wherein the first ion-exchange conditions include a temperature of from 50°F to 250°F and a sodium hydroxide solution concentration of from 0.5 to 10 wt.%.

4. A method as claimed in claims 1 to 3 wherein the sodium exchanged mass has a Na_2O/Al_2O_3 ratio greater than 0.7:1.

5. A method as claimed in any of claims 1 to 4 wherein the second ion-exchange conditions include a pH sufficient to preclude formation of the hydrogen form of the zeolite, and a temperature within the range of from 50°F to 250°F.

6. A method as claimed in any of claims 1 to 5 wherein the precursor mass comprises X zeolite and the sodium cations are essentially completely exchanged in step (b) with cations of one or more metals selected from lithium, rubidium, cesium, beryllium, magnesium, calcium, strontium, copper, and silver, with or without potassium and/or barium, or with potassium cations.

7. A method as claimed in any of claims 1 to 5 wherein the precursor mass comprises Y zeolite and the sodium cations are essentially completely exchanged with cations of one or more metals selected from lithium, beryllium, magnesium,

calcium, strontium, copper and silver, with or without potassium, rubidium, cesium and/or barium.

8. A method as claimed in claim 1 carried out substantially as hereinbefore specifically described or illustrated in any one of the foregoing Examples I to III.

9. A solid adsorbent whenever manufactured by a method as claimed in any preceding claim.

10. An adsorptive separation process wherein a fluid mixture of chemical compounds one of which is selectively preferentially adsorbed by an adsorbent as claimed in claim 9 is pressed through a bed of such an adsorbent under adsorption conditions and a fluid stream enriched in a selectively adsorbed or selectively non-adsorbed component is recovered.

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